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Preparation of a simple biocompatible magnetite@citric acid: An efficient reusable solid acid catalyst for the rapid synthesis of antipyrine Schiff's bases and study of their radical scavenging potential

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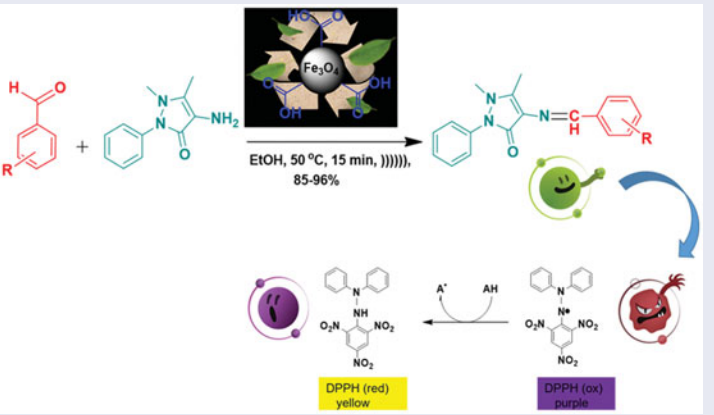
ABSTRACT

Citric acid immobilized magnetic nanoparticles (MNPs@CA) have been synthesized and used for the preparation of bio-important antipyrine **(1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one)** derived Schiff's bases **(3a–k)** in lesser reaction time with very high yield under ultrasonication. The catalyst was characterized by FT-IR, powder X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), and thermogravimetric analysis (TGA). The functionalized nanoparticles were easily separated using an external magnet during work-up procedure and show excellent reusability upto 8 cycles without any significant loss in catalytic activity. All the synthesized compounds **(3a–k)** were screened by DPPH (2,2-diphenyl-1-picrylhydrazyl) method with respect to ascorbic acid for their antioxidant activity and some of them gave promising results.

GRAPHICAL ABSTRACT



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Introduction

Nanotechnology is one of the most versatile areas of current research and wide range applications.

Their unique properties arise from particularly their high surface to volume ratio.[1–3] Various methods have been reported for their synthesis, among them the biological methods, plant mediated synthesis of nanoparticles are more attractive because of its simplicity, easy availability and stability of the resulting products.[4–12] Nowadays, they have attracted great deal of attention due to catalytic application such as synthesis of spirooxindoles,[13] carbonitriles,[14] 4-H chromenes,[15,16] decahydroacridine 1,8 diones,[17] oxidation of sulfides to sulfoxides,[18] synthesis of propargylamines,[19] quinoxaline,[20] etc.

Nanoparticles fill the gap between homogeneous and heterogeneous catalysis, but recovery by normal filtration technique limits their widespread utility which results in their loss disturbing the economics and sustainability of these nanocatalytic protocols.[21] In recent decades magnetic nanopartciles (MNPs) have gained popularity due to their ease of preparation and surface functionalisation, facile separation *via* magnetic force as well as low toxicity and price.[22] Bare MNPs due to their inherent instability and hydrophobic nature results in big clusters over time in the absence of any surface coating which reduces their surface energy.[23] Therefore it needs to be minimized by surface immobilization of MNPs with biocompatible organic and inorganic materials which protects them from being oxidized and provides them stability against damage during or after being used in organic transformations.[24,25] Surface functionalization of MNPs with PO_4^{3-}, sulfate and carboxylate are attractive surface modifications which can be easily accomplished. It is observed that carboxylate binding to MNPs is the strongest preventing leaching out during reaction, as well as protecting the bare NP's against damage hence it can be used undoubtedly in catalysis with good stability.[26]

Schiff bases are some of the most widely used organic compounds. They are used as pigments & dyes,[27] catalysts,[28] intermediates in organic synthesis[29] and a polymer stabilisers.[30] Recently they have been utilized for optical recording technology,[31] as electrical conductor, electrode materials, and micro-electronic equipment,[32] organic batteries or electrochromic display devices.[33] The Schiff's base of 4-amino antipyrine is considered to be pyrazolone derivatives and are reported to demonstrate biological, clinical, pharmacological and analytical applications.[34] Synthesis of Schiff's base is often carried out with or without acid catalyzed by various previously reported synthetic methods like microwave assisted,[35] irradiation by UV,[36] ultrasonication,[37] etc. The main drawback of these reported methods is the utilization of large amount of solvent and longer reaction time. Therefore there is need to vary or modify the conventional methods which are not eco-friendly and less efficient. Separation of the catalyst and final product from the reaction mixture is one of the most vital aspects of synthetic protocols. Catalytic recovery by filtration is relatively inefficient. Another technique, extractive isolation of products also requires excessive amount of organic solvents. The development of versatile and efficient procedures for the preparation of these types of compounds by using a new catalyst and active ongoing research area, and there will be a scope for further improvement towards lower-reaction times, improved yields and milder-reaction conditions. In view of this MNP@CA has been prepared by the

adsorption of citric acid on the surface of magnetite nanoparticles by co-ordinating whereby one or two of the carboxylate functionality co-ordinate depending upon steric necessity and the curvature of surface.[38] The catalytic property of MNP@CA for the activation of carbonyl group of aromatic aldehyde to obtain the desired compounds **(3a–k)** was successfully explored. Due to trouble free ease of separation using an external magnet, this method provides a rapid and effective way to synthesize Schiff's bases along with the added advantage of reusability and recyclability up to 8 runs without any significant loss of yield. In addition all the compounds were screened for radical scavenging potential by DPPH method taking ascorbic acid as standard[19]. Indeed, to the best of our knowledge this is the first report of hassle free synthesis of bio-important antipyrine Schiff's bases using MNP@CA. Antioxidants are molecules, which can safely interact with free radicals and terminate the chain reaction before vital molecules are damaged. Free radicals are major factors leading to more than sixty different health problems including ageing, cancer and atherosclerosis etc. Addition of hydrogen would remove the odd electron feature which is responsible for radical reactivity. The different synthesized compounds **3a–k** showed good antioxidant activity taking Ascorbic acid as standard in DPPH free radicals scavenging, which indicates that the compounds have potential to prevent free radical mediated oxidative damage.

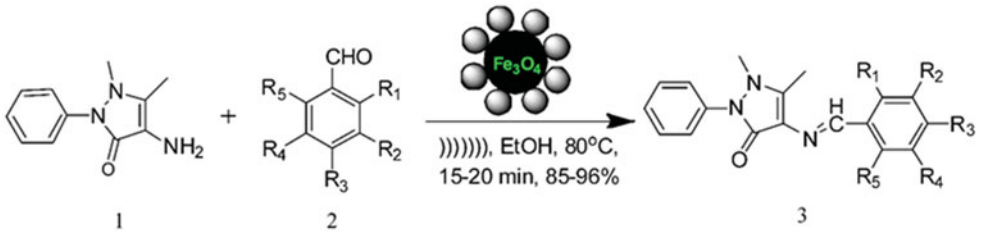
Results and discussions

Preparation of catalyst

Keeping our focus on the synthesis of MNPs and their post synthetic surface modification, we herein, report a method for the synthesis of nano MNP@CA. The magnetite nanoparticles were synthesized by chemical co-precipitation method similar to previously reported method with slight modification.[39] After that in order to improve the chemical stability, surface modification was performed by immobilization of citric acid on its surface.[26,40] (For details, please see supporting information). Figure SI1 gives a pictorial depiction for the synthesis of magnetic nano particles decorated by CA. Prepared catalyst (MNP@CA) was then characterized by using various microscopic and spectroscopic techniques such as FTIR (Figure SI2), FESEM (Figure SI3), XRD (Figure SI4), HRTEM (Figure SI5), TGA (Figure SI6).

Optimization studies

After characterization, catalytic activity of the magnetite@citric acid was assessed for synthesis of Schiff's base (Scheme 1). As shown in Table 1, initially a trial reaction has been carried out using benzaldehyde (1 mmol), 4 amino antipyrine (1 mmol) under ultrasonication at 50 °C with and without catalyst. When the reaction was performed in the absence of catalyst, the yield obtained was in traces (Table 1, entries 1 and 2). Further when the reaction was carried out by using 0.15 mol% of the catalyst under the same conditions, product was obtained with improved yield. Increased yield with MNP@CA may be attributed firstly due to the activation of carbonyl group of benzaldehyde through acidic proton of the carboxylic group of CA immobilized on magnetite and secondly due to the availability of enhanced surface area. The plausible mechanism



Scheme 1. Synthesis of Schiff's bases by using MNP@CA.

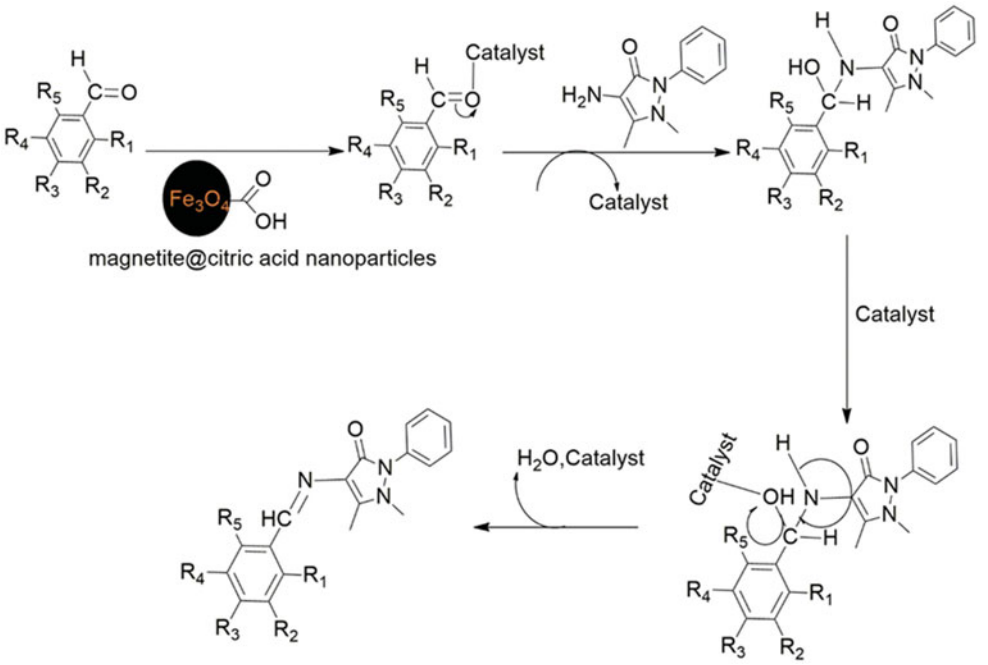
Table 1. Optimization for the synthesis of (E)-4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one under various reaction conditions.[a]

Experimental number	Catalyst (mol%)	Time	Temperature	Yield (%)[b]
1	No catalyst	15	50	28
2	No catalyst	120	50	42
3	No catalyst	120	80	44
4	0.25	15	50	58
5	0.25	30	50	64
6	0.25	60	50	64
7	0.25	60	80	65
8	0.45	15	50	66
9	0.45	30	50	68
10	0.45	60	50	70
11	0.45	60	80	72
12	0.65	15	50	90
13	0.65	30	50	92
14	0.65	60	50	94
15	0.65	15	80	95
16	0.80	15	50	92
17	0.80	30	80	94
18	0.80	60	80	94

[a]Reaction conditions: benzaldehyde (1 mmol), 4-amino antipyrine (1 mmol), solvent-ethanol (2 mL), 80 °C, ultrasonicated in open air.
[b]Isolated yield.
Without catalyst (Entries 1–3), With CA@magnetite nanocatalyst (Entries 4–18).
CA@magnetite as catalyst (Entries 3–14).

for the reaction given in the Scheme 2. Owing to the improved yield, the model reaction was performed using different mol% of the catalyst i.e. 0.25, 0.50, 0.65, 0.80 at different temperatures by varying the reaction time. Interestingly yield was increased up to 95% when 0.65 mol% of the catalyst was used (Table 1, entries 13, 14, and 15). With further increase of the catalyst to 0.80 mol%, efficiency did not change significantly. We have also studied individual effect of various reaction parameters as solvent standardization, catalyst loading and effect of temperature variation on % yield and the results proved that 0.65 mol % of catalyst, ethanol solvent and 80 °C of temperature ere the best optimized condition for the reaction (Figure SI7, Figure SI8, and Figure SI9).

With the optimal conditions in hand (Table 1, entry 15), we next studied the substrate scope of this reaction by screening the different aromatic benzaldehydes. A variety of different substituted aromatic aldehydes possessing electron withdrawing and electron donating groups gave good yield (86–96%). Several aromatic aldehydes containing electron releasing substituents, electron withdrawing substituents and halogens on their aromatic ring were utilized in the reaction and the corresponding products was obtained



Scheme 2. Plausible mechanism for the synthesis of Schiffs base by using MNP@CA.

Table 2. Synthesis of various Schiff's base using citric acid@magnetite.[a]

Entry	R_1	R_2	R_3	R_4	R_5	Time (min)	Yield (%)[b]
3a	H	H	H	H	H	15	95
3b	OH	H	H	H	H	20	90
3c	H	H	OH	H	H	20	90
3d	OH	H	OH	H	H	15	91
3e	OH	OCH_3	H	H	H	15	88
3f	OH	H	H	NO_2	H	10	96
3g	NO_2	H	H	H	H	10	96
3h	H	H	CN	H	H	15	92
3i	H	H	Cl	H	H	10	86
3j	OH	H	H	$N(C_2H_5)_2$	H	15	88
3k	2-hydroxy naphthaldehyde					10	92

[a]Reaction conditions: benzaldehyde (1 mmol), 4-amino antipyrine (1 mmol), solvent-ethanol (2 mL), 80 °C, 0.65 mol% of CA@magnetite nanocatalyst, ultrasonicated in open air.
[b]Isolated yield.

with high yields and in shorter reaction times. As evident from Table 2, ease of the reaction is directly related to the substituent on benzene ring. The electron withdrawing groups (such as nitro, cyano, halo) were found to activate the aldehydes towards nucleophilic attack and increases the reaction rate (Entry **3f, 3 g, 3 h, 3i**). The level of reusability of MNP@CA catalyst was also checked. For this the model reaction (benzaldehyde, 4-amino antipyrine) was examined under optimized conditions. When the reaction was completed, the catalyst was separated out using an external magnet and then thoroughly washed with hot ethanol (2 × 10 ml) and dried in an oven for 3 h at 80 °C and was used for next run. The recycled catalyst could be reused 8 times without any significant decrease in its catalytic activity (Figure SI10). MNP@CA NPs catalyst exhibits excellent activity and stability and herein we are giving the spectral information to demonstrate

the structural stability. FTIR analysis of magnetite@citric acid was carried out and it has been observed that the characteristics peak of citric acid immobilization on magnetite through carboxylate groups forming ester bond with the OH group present on the surface of magnetite comes at 1627 cm^{-1} and the symmetric vibration due to non-dissociated OH group of citric acid appeared at 3300 cm^{-1}. After eight runs same peaks were appeared but with lower intensity which might account for the gradual decrease in conversion over several cycles. These loses may result from the adhesion of insoluble catalyst to the surface of the round bottom flask or reaction vessel during the separation-recovery protocol. Almost the same characteristic peaks of magnetite@citric acid were obtained in Figure SI3 (B) (a) and (b) indicating that morphology and crystalline cubic spinel structure has been also preserved during catalytic reaction. SEM images of the magnetite@citric acid showed that the nanocatalyst was almost spherical in shape before and after the reaction again proved that the catalyst was structurally stable throughout the reaction and various runs. Figure SI3 (C) indicated the surface becomes more rough and seems exhausted after 8^{th} run which might be the reason for decrement of the product yield during subsequent cycles. By considering above spectral analysis it has been concluded that catalyst exhibits excellent activity stability.

Biological evaluation

All the compounds were screened for radical scavenging potential by DPPH method taking ascorbic acid as standard. The inhibitory effect of DPPH was calculated according to the following formula:

$$\text{Scavenging activity}(\%) = 100 \times \left(1-\left(A_{\text{sample}}/A_{\text{control}}\right)\right)$$

A_{control} is the absorbance of the control solution (containing all reagents except the compounds being tested) and A_{sample} is the absorbance of the test compound. IC_{50} of the samples were determined by the method described by Molyneux (2004). The IC_{50} value is the concentration of inhibitor at which 50% of the DPPH radicals are scavenged. A low IC_{50} value indicates a high ability of the compound to act as a DPPH scavenger (Figure 1). The effects of functional groups on activity of the diphenolic antioxidants were observed. Bond Dissociation Energy (BDE) is the amount of energy needed to break a given bond to produce two fragments (in this case AO-H → AO· + H). BDE is an important factor in determining the efficacy of an antioxidant since the weaker the OH bond, the faster will be the reaction with the free radicals. The addition of electron-donating substituents to an aromatic ring can increase radical scavenging activity as a result of increased electron density at carbon atoms in the ring.[41] In contrast, the presence of electron-withdrawing substituents decreases electron density around the ring, hence decreasing its ability to scavenge free radicals due to poor aromatic ring resonance of the phenoxyl radical. On the basis of above discussed factors, some of them **3c, 3i, 3d, 3g, 3b** gave very good results. The rest synthesized compounds showed average antioxidant activity taking ascorbic acid as standard in DPPH free radicals scavenging, which indicates that the compounds have potential to prevent free radical mediated oxidative damage.

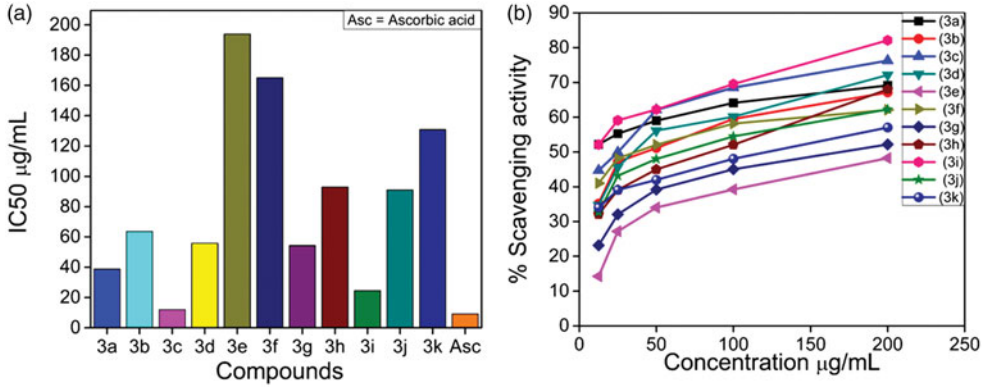


Figure 1. Antioxidant activity performance of synthesized Schiff's bases (**3a–3k**).

Reusability of catalyst

After each run of the reaction the catalyst was separated by using an external magnet and washed out thoroughly in a boiling tube filled with 10 ml of ethanol to remove any product sorbed inside or on the nano catalyst. It was then heated in an oven at 80 °C for 3 h and was used for the next run. It was observed that there was no significant loss in catalytic activity shown by the nano catalyst for subsequent eight cycles as shown in (Figure SI10).

Conclusion

We have developed a green protocol for the synthesis of biological active Schiff's base. These Schiff's bases have been synthesized using antipyrine and various aromatic aldehyde derivatives catalyzed by MNP@CA which has been recovered and reused upto 8 cycles without any significant loss in yield. On the basis of presented results, the investigated compounds **3a–k** can be considered as good source of antioxidants. This study could be beneficial for the development of such heterocyclic moiety containing derived compounds for pharmaceutical applications.

Experimental methods

General remarks

All chemicals and solvents purchased are of analytical grade and used without further purification. Melting points were determined in open glass capillaries and are reported uncorrected. Infrared spectra were collected on a Bruker Fourier transform infrared spectrophotometer (FTIR) (Alpha) with pressed KBr pellets. ^{1}H NMR and ^{13}C NMR were recorded on a Jeol ECS 400 and 100 MHz spectrophotometer using DMSO d_6 as a solvent. Ultrasonic bath; Elma S 70 H with 37 KHz was used. SEM was recorded on (FESEM; NOVA nano SEM, 10 kV), TEM was recorded on Tecnai G^2 20 (FEI) S-Twin, 100 kV, XRD was obtained with X-ray Diffractometer (Panalytical X Pert Pro) using Cu Kα radiation. Thermo gravimetric analysis (TGA) was performed on a Mettler thermal

analyzer in an inert atmosphere at a heating rate of 10 °C/min. UV-vis study was done by Double Beam UV-vis Spectrophotometer (Spectrascan UV-2600, Chemito).

Synthesis of (E)-4-((2-methylbenzylidene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (3a)

Initially benzaldehyde (1 mmol) dissolved in 3 ml of ethanol was taken in a 50 ml round bottom flask and 0.65 mol % of the catalyst was added to it which was then sonicated for 2 min to activate the carbonyl group of the benzaldehyde by the MNP@CA nano catalyst. Then 1 mmol 4-amino antipyrine was added to the reaction mixture and sonication continued till the completion of the reaction indicated by TLC (8:2 petroleum ether: ethyl acetate). The catalyst was then separated by using a strong external magnet. The reaction mixture was concentrated in a rota vapor under reduced pressure. The final solid of the desired product was obtained which was further purified by recrystallization using ethanol as a solvent. The solid catalyst was washed with hot EtOH and then dried in oven to reuse.

4 -(Benzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one (3a)

Off white solid, yield: 95%, mp found: 177–178 °C, reported: 178–179 °C.[42] IR (KBr):1643 (>C=O), 1560 (>C=N) cm^{-1}, ^{1}H NMR (400 MHz, DMSO d_6): $\delta = 9.55$ (–N=CH–, s), 7.81–7.32 (m, Ar 9H), 3.14 (s, –N–CH_3, 3H), 2.45 (s, 3 H, =C–CH_3), ^{13}C NMR (100 MHz, DMSO d_6) $\delta = 10.29$, 35.86, 116.82, 125.11, 127.41, 127.91, 129.26, 129.67, 130.68, 135.08, 138.04, 152.76, 154.83, 160.12, HRMS (ESI) ($C_{18}H_{17}N_3O$) $[M + H]^+$ calcd. 292.1445; found: 292.1442

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